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# COPPER OXIDE SUPERCONDUCTORS

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WILEY

A Wiley-Interscience Publication

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*Library of Congress Cataloging in Publication Data:*

Poole, Charles P.

Copper oxide superconductors / Charles P. Poole, Jr., Timir Datta, and Horacio A. Farach; with help from M. M. Rigney and C. R. Sanders.  
p. cm.

"A Wiley-Interscience publication."

Bibliography: p.

Includes index.

1. Copper oxide superconductors. I. Datta, Timir. II. Farach, Horacio A. III. Title.

QC611.98.C64P66 1988  
539.6'23-dc 19 88-18569 CIP  
ISBN 0-471-62342-3

Printed in the United States of America

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# V

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## PREPARATION AND CHARACTERIZATION OF SAMPLES

### A. INTRODUCTION

Copper oxide superconductors with a purity sufficient to exhibit zero resistivity or to demonstrate levitation (Early) are not difficult to synthesize. We believe that this is at least partially responsible for the explosive worldwide growth in these materials. Nevertheless, it should be emphasized that the preparation of these samples does involve some risks since the procedures are carried out at quite high temperatures, often in oxygen atmospheres. In addition, some of the chemicals are toxic, and in the case of thallium compounds the degree of toxicity is extremely high so ingestion, inhalation, and contact with the skin must be prevented.

The superconducting properties of the copper oxide compounds are quite sensitive to the method of preparation and annealing. Multiphase samples containing fractions with  $T_c$  above liquid nitrogen temperature (Monec) can be synthesized using rather crude techniques, but really high-grade single-phase specimens require careful attention to such factors as temperature control, oxygen content of the surrounding gas, annealing cycles, grain sizes, and pelletizing procedures. The ratio of cations in the final sample is important, but even more critical and more difficult to control is the oxygen content. However, in the case of the Bi- and Tl-based compounds, the superconducting properties are less sensitive to the oxygen content.

Figure V-1 illustrates how preparation conditions can influence superconducting properties. It shows how the calcination temperature, the annealing time, and the quenching conditions affect the resistivity drop at  $T_c$  of a BiSrCa-CuO pellet, a related copper-enriched specimen, and an aluminum-doped coun-

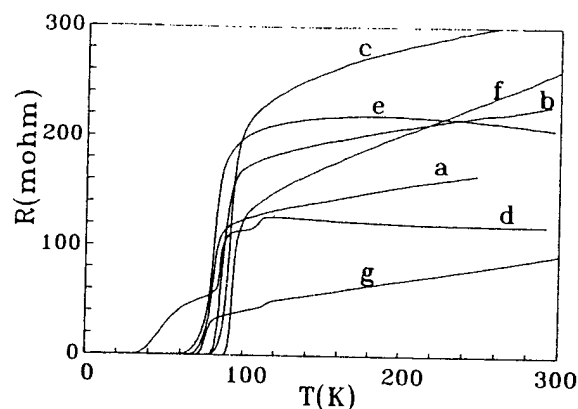


Fig. V-1. Effects of heat treatments on the resistivity transition of  $\text{BiSrCaCuO}_{7-\delta}$  (a) calcined at  $860^\circ\text{C}$ , (b) calcined at  $885^\circ\text{C}$ , (c) calcined at  $901^\circ\text{C}$ , (d) aluminum-doped sample calcined at  $875^\circ\text{C}$ , prolonged annealing, (e) copper-rich sample calcined at  $860^\circ\text{C}$ , (f) aluminum-doped sample calcined at  $885^\circ\text{C}$ , slow quenching and (g) calcined at  $885^\circ\text{C}$ , prolonged annealing, and slow quenching (Chuz5).

terpart (Chuz5). These samples were all calcined and annealed in the same temperature range and air-quenched to room temperature.

Polycrystalline samples are the easiest to prepare, and much of the early work was carried out with them. Of greater significance is work carried out with thin films and single crystals, and these require more specialized preparation techniques. More and more of the recent work has been done with such samples.

Many authors have provided sample preparation information, and others have detailed heat treatments and oxygen control. Some representative techniques will be discussed.

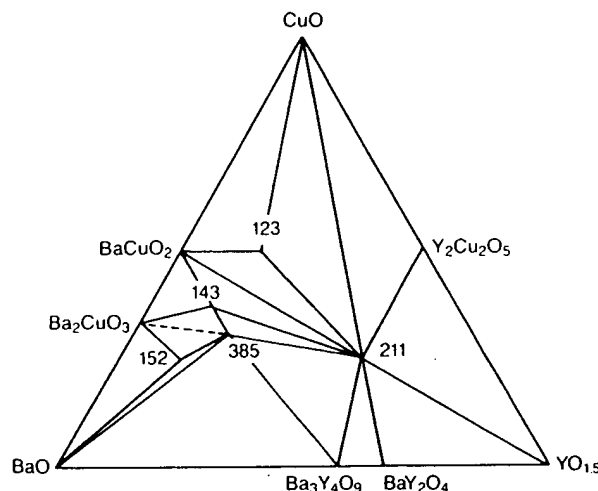
The beginning of this chapter will treat methods of preparing bulk superconducting samples in general, and then samples of special types such as thin films and single crystals. The remainder of the chapter will discuss ways of checking the composition and quality of the samples. The thermodynamic or subsolidus phase diagram of the ternary Y-Ba-Cu oxide system illustrated in Fig. V-2 contains several stable stoichiometric compounds such as the end-point oxides  $\text{Y}_2\text{O}_3$ ,  $\text{BaO}$ , and  $\text{CuO}$  at the apices, the binary oxides stable at  $950^\circ$ , ( $\text{Ba}_3\text{CuO}_4$ ),  $\text{Ba}_2\text{CuO}_3$ ,  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{Cu}_2\text{O}_5$ ,  $\text{Y}_4\text{Ba}_3\text{O}_9$ ,  $\text{Y}_2\text{BaO}_4$ , and ( $\text{Y}_2\text{Ba}_4\text{O}_7$ ), along the edges, and ternary oxides such as ( $\text{YBa}_3\text{Cu}_2\text{O}_7$ ), the semiconducting green phase  $\text{Y}_2\text{BaCuO}_5$ , and the superconducting black solid  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  in the interior (Beye2, Bour3, Capo1, Eagl1, Frase, Hosoy, Jone1, Kaise, Kurth, Kuzzz, Leez3, Lian1, Mali1, Schni, Schn1, Schu1, Takay, Torra, Wagne). Compounds in parentheses are not on the figure, but are reported by other workers. The existence of a narrow range of solid solution was reported (Panso), and then argued against (Wagne) by the same group.

Fig. V-2. Ternary phase diagram of the  $\text{Y}_2\text{BaCuO}_5$  system and other compounds.

## B. METHODS

In this section the various solid-state techniques used in the preparation of superconducting samples are discussed. The processes in superconductors are discussed at the atomic scale and some familiar processes are more competent.

In the solid-state, the desired compounds of Sr, Tl, Y, or other oxides in nitric



Compound	Slowly cooled to room temperature
123 - $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+\delta}$	$\text{O}_7$
143 - $\text{YBa}_4\text{Cu}_3\text{O}_{8.5+\delta}$	$\text{O}_9$
385 - $\text{Y}_3\text{Ba}_8\text{Cu}_5\text{O}_{17.5+\delta}$	$\text{O}_{18}$
152 - $\text{YBa}_5\text{Cu}_2\text{O}_{8.5+\delta}$	$\text{O}_9$
211 - $\text{Y}_2\text{BaCuO}_5$	
$\text{Ba}_2\text{CuO}_{3+\delta}$	$\text{O}_{3.3}$

Fig. V-2. Ternary phase diagram of the  $\text{Y}_2\text{O}_3$ -BaO-CuO system at  $950^\circ\text{C}$ . The green phase [ $\text{Y}_2\text{BaCuO}_5$ , (211)] the superconducting phase [ $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ , (123)], and three other compounds are shown in the interior of the diagram (DeLee).

## B. METHODS OF PREPARATION

In this section three methods of preparation will be described, namely, the solid state, the coprecipitation, and the sol-gel techniques (Hatfi). The widely used solid-state technique permits off-the-shelf chemicals to be directly calcined into superconductors, and it requires little familiarity with the subtle physicochemical processes involved in the transformation of a mixture of compounds into a superconductor. The coprecipitation technique mixes the constituents on an atomic scale and forms fine powders, but it requires careful control of the pH and some familiarity with analytical chemistry. The sol-gel procedure requires more competence in analytical procedures.

In the solid-state reaction technique one starts with oxygen-rich compounds of the desired components such as oxides, nitrates, or carbonates of Ba, Bi, La, Sr, Tl, Y, or other elements. Sometimes nitrates are formed first by dissolving oxides in nitric acid and decomposing the solution at  $500^\circ\text{C}$  before calcination

$\text{LaSrCaCuO}_{7-\delta}$  (a) aluminum-doped sample calcined at and (g) calcined

the same tem-

the early work l out with thin paration tech- ch samples. n, and others entative tech-

bulk supercon- h as thin films ys of checking or subsolidus Fig. V-2 con- l-point oxides  $\text{O}_7$ , ( $\text{Ba}_2\text{CuO}_4$ ),  $\text{O}_9$ ), along the ig green phase n the interior urth, Kuzzz, ). Compounds workers. The so), and then

(e.g., Davis, Holla, Kelle). These compounds are mixed in the desired atomic ratios and ground to a fine powder to facilitate the calcination process. Then these room-temperature-stable salts are reacted by calcining for an extended period ( $\approx 20$  hr) at elevated temperatures ( $\approx 900^\circ\text{C}$ ). This process may be repeated several times, with pulverizing and mixing of the partially calcined material at each step. As the reaction proceeds, the color of the charge changes. The process usually ends with a final oxygen anneal followed by a slow cool down to room temperature of the powder, or pellets made from the powder, by sintering in a cold or hot press. Sintering is not essential for the chemical process, but for transport and other measurements it is convenient to have the material pelletized. A number of researchers have provided information on this solid-state reaction approach (e.g., Allge, Finez, Galla, Garla, Gopal, Gubse, Hajk1, Hatan, Herrm, Hikal, Hirab, Jayar, Maen1, Mood1, Mood2, Neume, Poepp, Polle, Qadri, Rhyne, Ruzic, Saito, Sait1, Sawa1, Shamo, Takit, Tothz, Wuzz3).

Some of the earlier works on foils, thick films, wires, or coatings employed a suspension of the calcined powder in a suitable organic binder, and the desired product was obtained by conventional industrial processes such as extruding, spraying, or coating.

In the second or coprecipitation process the starting materials for calcination are produced by precipitating them together from solution (e.g., Asela, Bedno, Leez7, Wang2). This has the advantage of mixing the constituents on an atomic scale. In addition the precipitates may form fine powders whose uniformity can be controlled, which can eliminate some of the labor. Once the precipitate has been dried, calcining can begin as in the solid-state reaction procedure. A disadvantage of this method, at least as far as the average physicist or materials scientist is concerned, is that it requires considerable skill in chemical procedures.

Another procedure for obtaining the start-up powder is the sol-gel technique in which an aqueous solution containing the proper ratios of Ba, Cu, and Y nitrates is emulsified in an organic phase and the resulting droplets are gelled by the addition of a high-molecular-weight primary amine which extracts the nitric acid. This process was initially applied to the La materials, but has been perfected for YBaCuO as well (Cimaz, Hatfi).

When using commercial chemical supplies to facilitate the calcination process a dry or wet (acetone) pregrinding with an agate mortar and pestle or a ball mill is recommended. Gravimetric amounts of the powdered precursor materials are thoroughly mixed and placed in a platinum or ceramic crucible. Care must be taken to ensure the compatibility of the ceramic crucible with the chemicals to obviate reaction and corrosion problems.

Complete recipes for the YBa\* material have been described (e.g., Gran2). Typically, the mixture of unreacted oxides is calcined in air or oxygen around  $900^\circ\text{C}$  for 15 hr. During this time the YBaCuO mixture changes color from the green  $\text{Y}_2\text{BaCuO}_5$  phase to the dark gray  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compound. Then the charge is taken out, crushed, and scanned with X rays to determine its purity. If warranted by the powder pattern X-ray scan, the calcination process is repeated. Often, at this stage the material is very oxygen poor, and electrically it is semi-

conducting or sintered for s at  $\approx 3^\circ\text{C}/\text{min}$  temperature is in conductor phase quenching. T sand blasting another oxygen serve the sup

An example metric amounting them in a dures several same temperature shows the e curve.

**WARNING:**  
precautions in the high-temperature oxides in air are powdered, and cutes in flow. perature (Sh Allen Hei mation on t Pharmacol. antidote for cusses cases

## C. ADDITIONAL

This section the preparation

In one example were calcined compression (Graham). The 1100°C. Sh for YBa\* are distinct from

Another or Yb, Ba, tained sub

conducting or even nonconducting. After pelletizing at  $>10^5$  psi the pellet is sintered for several hours at  $\approx 900^\circ\text{C}$  in flowing oxygen and then slowly cooled at  $\approx 3^\circ\text{C}/\text{min}$  down to room temperature. Slow cooling from the elevated temperature is important for producing the low-temperature orthorhombic superconductor phase. The tetragonal nonsuperconducting phase may be obtained by quenching. The pellet may be used as is or it may be cut into suitable sizes by sand blasting, with a diamond saw, or with an arc. After vigorous machining another oxygen anneal ( $450^\circ\text{C}$ , 1 hr, slow cool down) is often required to preserve the superconducting properties.

An example of preparing a Bi-based superconductor involves mixing gravimetric amounts of high-purity  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$ , and  $\text{CuO}$  powders, calcining them in air at  $750$ – $890^\circ\text{C}$ , regrinding them, and then repeating these procedures several times. Then pellets of the calcined product were sintered at the same temperature and quenched to room temperature (Chuz5). Figure V-1 shows the effect of sample treatment on the resistance versus temperature curve.

**WARNING:** As was mentioned above, thallium is a toxic material and proper precautions must be taken when working with it. It is useful to start by preparing the high-quality precursor compound  $\text{BaCu}_3\text{O}_4$  or  $\text{Ba}_2\text{Cu}_3\text{O}_5$  by reacting the oxides in air at  $925^\circ\text{C}$  for 24 hr. Then appropriate amounts of  $\text{Tl}_2\text{O}_3$  are added, powdered, and pelletized. The pellet is then heated to  $880$ – $910^\circ\text{C}$  for a few minutes in flowing oxygen, and at the onset of melting it is quenched to room temperature (Shen1).

Allen Hermann has suggested consulting the following references for information on thallium poisoning and antidotes thereto: H. Heydlauf, *Euro. J. Pharmacol.* 6, 340 (1969), which discusses thallium poisoning and describes the antidote ferric cyanoferrate, and *Int. J. Pharmacol.* 10, 1 (1974), which discusses cases of thallium intoxication treated with Prussian Blue.

## C. ADDITIONAL COMMENTS ON PREPARATION

This section will treat some additional methods which have been employed for the preparation of samples.

In one experiment coprecipitated nitrates of La, Sr, Cu, and Na carbonate were calcined for 2 hr at  $825^\circ\text{C}$ , pressed into pellets, and then subjected to shock compression of  $\approx 20$  GPa at an estimated peak temperature of  $\approx 1000^\circ\text{C}$  (Graha). The best superconductivity was observed after 1 hr of air exposure at  $1100^\circ\text{C}$ . Shock compression fabrication has also been reported (Murrz, Murr1) for  $\text{YBa}_*$  and other rare-earth derivatives. This process produced "monoliths," distinct from the usual composites.

Another technique involved the formation of a precursor alloy of Eu, Ba, Cu or Yb, Ba, Cu by rapid solidification, with the superconducting materials obtained subsequently by oxidation (Halda). A novel method involved preparing

the superconductors from molten Ba-Cu oxides and solid rare-earth-containing materials. In principle this process may be better controlled and complicated shapes can be molded or cast (Herma).

Pulsed current densities of  $300\text{--}400 \text{ \AA}/\text{cm}^2$  with rise times of  $0.6 \mu\text{sec}$  at room temperature were used to convert the weakly semiconducting phase of YBaCuO to the stable metallic phase (Djure, Djuric).

A claim was made that thermal cycling from cryogenic temperatures to 240 K raised the  $T_c$  of YBa\* and YBaCuO-F (with some F substituting for O) to 159 K. Cycling above 140 K lowered  $T_c$ . This cycling process could possibly change the density of twins and thereby enhance  $T_c$ .

A freeze-drying technique was reported as producing sintered materials homogeneous in composition and small in porosity (Stras). The low-temperature firing of oxalates ( $T < 780^\circ\text{C}$ ) has also been reported as producing a homogeneous material of small grain size (Manth).

Both Bi and Pb act as fluxes during the sintering process (Kilco). Bismuth substitution appears to reduce the normal state resistivity by about an order of magnitude without affecting the superconducting properties.

A convenient method of separating the superconducting particles from a powdered mixture using magnetic levitation has been reported (Barso). This may be used to select the superconducting fraction after each calcination process.

#### D. FILMS

The new ceramic oxide superconductors presently lack mechanical properties such as ductility which are needed for high-current applications like magnet wire fabrication (Jinzz-Jinz3) and power transmission. To circumvent some of these deficiencies for microelectronic applications one can prepare thin films on suitable substrates. Some devices such as Josephson junctions require thin superconducting films. Many workers have discussed the preparation and properties of LaSrCuO- (e.g., Adach, Delim, Kawas, Koinu, Matsu, Nagat, Naito, Tera1) and YBaCuO- (e.g., Burbi, Charz, Evett, Gurvi, Hause, Hongz, Inamz, Kwozz, Kwoz1, Manki, Scheu, Somek, Wuzz4) type films.

Almost every conceivable thin-film deposition technique such as electron beam evaporation, molecular beam epitaxy, sputtering, magnetron, laser ablation, screening, and spraying has been tried with the copper oxide system. Some of these techniques require expensive, elaborate apparatus, although descriptions of simple thin-film deposition systems are also available (e.g., see Koin1). Some representative examples of deposition procedures will be discussed.

Epitaxial films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  on (100)  $\text{SrTiO}_3$  were produced using three separate electron beam sources (e.g., Chaud, Chau1, Laibo). The deposition was done in  $10^{-4}\text{--}10^{-3}$  torr  $\text{O}_2$  with a substrate temperature of  $400^\circ\text{C}$ . The deposited films were atomically amorphous with a broad X-ray peak. The epitaxial ordering was achieved upon annealing in  $\text{O}_2$  at  $900^\circ\text{C}$  with the orthorhombic  $c$  axis essentially perpendicular to the plane.

High-quality beam to evaporation (Hammo, O) ited film in oxygen  $750^\circ\text{C}$  for 1 hr, furnace.

Superconducting (Mac) was Ar or an Ar- $10^{-7}$  torr and, with  $\text{ZrO}_2\text{--}9\% \text{ Y}_2\text{O}_3$  films. The films given annealing. Properties depended on conditions, com

Films of dysprosium beam epitaxy (N) cess was monitored copper was incorporated amorphous Ba a high-temperature

Films of  $\text{Y}_{1.1}\text{I}$  ness of  $500 \text{ \AA}$  was ited on  $\text{SrTiO}_3$ , pellet of YBaCuO. The evaporation  $6 \text{ Hz}$ ,  $\approx 30 \text{ nsec}$  heated to  $450^\circ\text{C}$  they appeared slightly oxygen annealed hours. Standard superconductivity tivity achieved r LaSr\* (Moorj) a

Films were of and Cu in layer  $200^\circ\text{C}$  and  $10^{-5}$  layers to diffuse ducting compound conductivity was  $\text{Y}_2\text{O}_3$ , and BaCO

Some  $5000\text{--}\text{\AA}$  vacuum dc-magnet was  $0.2 \text{ \AA}/\text{sec}$ , strate distance



High-quality superconducting films were obtained using a multiple electron beam to evaporate metallic sources in a flow of molecular oxygen at  $4-5 \times 10^{-6}$  torr (Hammo, Ohzzz). The deposition rate was  $10 \text{ \AA/sec}$ . To anneal the deposited film in oxygen it was heated for 3-6 hr in a flow of oxygen at  $650^\circ\text{C}$ , raised to  $750^\circ\text{C}$  for 1 hr, then to  $850^\circ\text{C}$  for 1 hr, and finally slowly cooled down in the furnace.

Superconducting films were prepared using a double ion beam sputtering arrangement (Madak). The target beam was Ar at 40 mA, and the substrate beam was Ar or an Ar- $\text{O}_2$  mixture at 10-500 eV and 2 mA. The base pressure was  $5 \times 10^{-7}$  torr and, with the gas,  $4 \times 10^{-4}$  torr. The best substrate materials such as  $\text{ZrO}_2$ -9%  $\text{Y}_2\text{O}_3$  did not appreciably interact, diffuse, or change the deposited films. The films were  $\approx 1 \text{ }\mu\text{m}$  thick and were rendered superconducting by oxygen annealing. Zero resistance was attained at 88 K. The superconducting properties depended upon the ion beam energy, substrate temperature, annealing conditions, composition, and the extent of poisoning from the substrate.

Films of dysprosium barium copper oxide were grown (Webbz) by molecular beam epitaxy (MBE) using a Varian 360 MBE system, and the nucleation process was monitored by reflection high-energy electron diffraction (RHEED). The copper was incompletely oxidized in metallic microcrystals growing in a sea of amorphous Ba and Dy. After deposition superconducting films were obtained by high-temperature oxygen annealing.

Films of  $\text{Y}_{1.1}\text{Ba}_{1.5}\text{Cu}_3\text{O}_{6.4}$  approximately 3300  $\text{\AA}$  thick with a surface roughness of 500  $\text{\AA}$  were prepared (Dijkk, Inamz, Wuzz4). These films were deposited on  $\text{SrTiO}_3$ , sapphire, and vitron carbon by evaporation from a single bulk pellet of YBaCuO 1 cm diameter and 0.2 cm thick at a pressure of  $5 \times 10^{-7}$  torr. The evaporation was produced by several thousand pulses of laser irradiation (3-6 Hz,  $\approx 30 \text{ nsec}$  width,  $1 \text{ J/pulse}$ ,  $2 \text{ J/cm}^2$ ). For best results the substrate was heated to  $450^\circ\text{C}$ . As deposited thin films were well bonded to the substrate and they appeared shiny dark brown and were electrically insulating. The films were oxygen annealed at  $900^\circ\text{C}$  for 1 hr and then slowly cooled over a period of several hours. Standard four-probe resistivity measurements indicated the onset of superconductivity around 95 K and, for a (100)  $\text{SrTiO}_3$  substrate, with zero resistivity achieved near 85 K. The laser ablation technique was also employed for LaSr\* (Moorj) and YBa\* (Nara1).

Films were obtained from sandwiched multilayers by depositing  $\text{Y}_2\text{O}_3$ , BaO, and Cu in layers (Nasta, Tsaur) on  $\text{ZrO}_2$ , MgO, and sapphire substrates at  $200^\circ\text{C}$  and  $10^{-5}$  torr. Oxygen treatment for 1-2 hr at  $\approx 850^\circ\text{C}$  permitted the layers to diffuse, homogenize, and oxygenate, and thereby form the superconducting compound (Baozz). Films on Ni have also been reported in which superconductivity was obtained by a diffusion process involving the Cu substrate,  $\text{Y}_2\text{O}_3$ , and  $\text{BaCO}_3$  composite (Tachi).

Some 5000- $\text{\AA}$  thick films of YBaCuO have been deposited using an ultrahigh vacuum dc-magnetron getter-sputter deposition system. The deposition rate was  $0.2 \text{ \AA/sec}$ , the substrate temperature was  $1050^\circ\text{C}$ , and the target-to-substrate distance was 12 cm. The scattering was done in an Ar- $\text{O}_2$  atmosphere.

The X-ray and electron microscope examinations indicated some variation among the substrates arranged on the heater. Inhomogeneities were observed even within the film made on a single substrate. As deposited the films were oxygen deficient, and annealing produced suitable compositions. The reversible oxygen incorporation was monitored by the systematic splitting of the strongest X-ray peaks. The oxygen diffusion coefficient at 600°C was  $10^{-15}$  m<sup>2</sup>/sec and the activation energies for desorption and absorption were 1.1 and 1.7 eV, respectively. The highest onset temperature was 99 K with complete superconduction at 40 K. Exposure to water inhibited the superconductor (Barns, Kishi, Yanzz). A device structure with a Y<sub>2</sub>O<sub>3</sub> barrier has also been studied (Blami).

Another work showed that films produced by dc magnetron sputtering are copper deficient if the substrate-to-target distance is large or if the substrate is at an elevated temperature (Leez5).

Superconducting YBaCuO thin films with a large surface area ( $\approx 5$  cm  $\times$  5 cm) were grown on Al<sub>2</sub>O<sub>3</sub>, sapphire, and MgO up to a 500°C substrate temperature by magnetron and diode techniques. Rutherford back scattering (RBS) indicated a uniform composition across magnetron-deposited film areas with diameters up to 5 cm, and the diode film composition homogeneity was even better, but over a smaller area ( $\approx 2.5$  cm diameter). The as-deposited films were annealed in oxygen at different temperatures and exposure times. Prolonged high-temperature annealing ( $> 850^\circ\text{C}$ ) increased the impurity phase. The highest  $T_c$  films had a wide range of composition, with the maximum  $T_c$  film copper rich. On the basis of an in-situ resistivity study of YBa\* thin films a rapid heating to about 900°C in flowing helium followed by slow cool down in flowing oxygen was recommended (David).

The post-deposition anneal cycle was avoided by producing the films in a high-pressure reactive evaporation process involving rapid thermal annealing (Lathr). Smooth films were obtained on zirconia and SrTiO<sub>3</sub> substrates. Screen printing of oxide superconducting films is also possible (Budha, Fuzz1), and simple spray deposition has been reported (Gupta). Films have also been made by coating and spinning off the solutions. Aqueous and aqueous-alcoholic mixed solutions of the metal nitrates (Coop2), metal acetates in dilute acetic acid (Rice1), and sol-gels (Kram1) have all been reported. These processes are potentially important for commercial superconducting coatings on silicon (Kram1), on yttrium-stabilized zirconia (YSZ), on SrTiO<sub>3</sub> (Coop2, Gupta), and on MgO (Gupta, Rice1).

## E. SINGLE CRYSTALS

The bulk properties of oxide superconductors are averages over components parallel and perpendicular to the Cu-O planes. In addition, for orthorhombic samples there is an averaging over properties that differ for the  $a$  and  $b$  directions in this plane. This in-plane anisotropy is especially pronounced for the YBa\* 123 structure in which the Cu-O-Cu-O chains lie along the  $b$  axis. The

best way to use crystals. Uniaxial anisotropy causes twinning problems in single crystals.

A number of X-ray diffraction (e.g., Crabtree), and micro-Raman spectroscopy describe how to grow single crystals.

Millimeter-wave oxide flux (L. Taka4, Zhou) contamination a hot press oven (Satoz).

Small single crystals which were sphere and the structure also promotes melting a single crystal followed by liquid.

A gold crucible ( $1 \times 2 \times 0.1$  cm) was heated in a 400°C at 25°C on the surface of the crucible.

A detailed crystal by the 1:3 and 2:5 multistep method found at the crucibles. Placed crucibles were reported. A single DyBa\* as large

## F. ALIGNMENT

Clearly high quality of superconductors

some variation were observed in the films were . The reversible of the strongest  $m^2/\text{sec}$  and the 1.7 eV, respectively (Kishi, Yanzz). sputtering are e substrate is at

area ( $\approx 5 \text{ cm} \times$  substrate temper- sputtering (RBS) in areas with di- ty was even bet- sited films were mes. Prolonged phase. The high-  $T_c$  film copper ns a rapid heat- in flowing oxy-

g the films in a normal annealing substrates. Screen (a, Fuzz1), and also been made aqueous-alcoholic dilute acetic acid essences are poten- silicon (Kram1), o), and on MgO

over components or orthorhombic e  $a$  and  $b$  direc- ounced for the the  $b$  axis. The

best way to understand these materials is through experiments on perfect single crystals. Unfortunately, untwinned YBa\* crystals are not available so the  $a, b$  anisotropy cannot be resolved. Tetragonal superconductors should not have this twinning problem. In this work twinned monocrystals will be referred to as single crystals.

A number of experiments have been carried out on monocrystals such as X-ray diffraction (e.g., Borde, Hazen, Lepad, Siegr, Onoda), magnetic studies (e.g., Crabt, Schn1, Worth), mechanical measurements (e.g., Cookz, Dinger), and micro-Raman spectroscopy (e.g., Hemle). In this section we will briefly describe how such crystals are made. The December 1987 issue of the *Journal of Crystal Growth* was devoted to superconductors.

Millimeter-size  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$  single crystals were grown in a molten copper oxide flux (Kawa1). Another basic technique employs other fluxes (Haned, Taka4, Zhou1), namely,  $\text{PbF}_2$ ,  $\text{B}_2\text{O}_3$ ,  $\text{PbO}$ ,  $\text{PbO}_2$ , with the risk of possible Pb contamination. LaSr\* crystals were also grown by the solid phase reaction using a hot press of pellets (Iwazu) and rapid quenching of a nonstoichiometric melt (Satoz).

Small single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  have been prepared from a sintered powder which was formed into a pellet and then heated, first in a reducing atmosphere and then in an oxidizing one at  $925^\circ\text{C}$ . Annealing a stoichiometric mixture also produced monocrystals (Liuzz). Millimeter-size crystals were grown by melting a stoichiometric mixture of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  plus excess  $\text{CuO}$  at  $1150^\circ\text{C}$  followed by holding at  $900^\circ\text{C}$  for 4 days (Damen, see also Fine1).

A gold crucible on a gold or alumina sheet was used to obtain free-standing ( $1 \times 2 \times 0.1 \text{ mm}$ ) single crystals of YBa\* (Kaise, Kais1, Holtz). A charge of 2 g was heated in air at  $200^\circ\text{C}/\text{hr}$  and held at  $975^\circ\text{C}$  for 1.5 hr, then it was cooled to  $400^\circ\text{C}$  at  $25^\circ\text{C}/\text{hr}$ . The molten charge creeps and forms single crystals and twins on the surfaces. The larger crystals formed in the space between the bottom of the crucible and the gold support sheet.

A detailed account has appeared of the preparation of a 123 compound single crystal by the flux method (Zhou1). The flux mole ratio  $\text{BaO}_2:\text{CuO}$  was between 1:3 and 2:5, and the nutrient  $\text{Y}_2\text{O}_3:\text{BaO}_2:\text{CuO}$  mole ratios were 0.5:2:3. A multistep temperature process was employed. Black single crystals of YBa\* were found at the bottom and at the edge between the wall and the bottom of the crucibles. Platinum crucibles seemed to contaminate the samples so alumina crucibles were recommended. Crystals as large as  $2 \times 2 \times 0.3 \text{ mm}^3$  were reported. A similar technique was used to produce single crystals of YBa\* and DyBa\* as large as 4 mm (Schn1).

## F. ALIGNED GRAINS

Clearly high-quality single crystals are important for understanding the physics of superconductors. However, much useful information about anisotropies can

be obtained by studying the properties of aligned grains, which are much easier to fabricate.

A superconducting sample can be initially a collection of randomly oriented grains, but various techniques can be used to partially orient these grains so that the *c* axis lies preferentially in a particular direction. For example uniaxial compression tends to orient compacted grains, with compressed 90- $\mu\text{m}$  particles exhibiting more alignment than compressed 10- $\mu\text{m}$  particles (Glowa). Epoxy-embedded grains have been aligned under the influence of an applied magnetic field and pressure (Arend).

X-ray and magnetic measurements have been reported on aligned crystalline grains of YBa\* (Farr<sup>1</sup>). Optical studies have also been made on aligned grains. The critical current density for samples cut parallel to the compression axis of such grains was nearly isotropic with respect to the direction of an applied magnetic field, and it was a factor of 6 smaller than that for the samples cut perpendicular to this axis (Glowa).

## G. REACTIVITY

The oxide superconductors are not inert materials, but rather they are sensitive to exposure to certain gases and to surface contact with particular materials. Great care must be exercised to avoid contamination from water vapor and carbon dioxide in the atmosphere. In addition these materials are catalytic to oxygenation reactions, and these factors result in the occurrence of various chemical and other interactions, especially at elevated temperatures. The granular and porous nature of the materials has an accelerating effect on such reactions.

Samples of YBaCuO may degrade in a matter of days when exposed to an ordinary ambient atmosphere; they react readily with liquid water, acids, and electrolytes, and moderately with basic solutions. The reaction with water (Barns, Kishi, Yanzz) produces nonsuperconducting cuprates. The effects of acetone and other organics (McAnd) have been determined, and stable carboxyl groups have been found in the YBaCuO lattice (Parmi).

Hydrogen enters the YBaCuO lattice at elevated temperatures and forms a solid solution. Low concentrations have very little effect and high concentrations degrade the superconducting properties (Berni, Reill, Yang3). The effects of exposure to oxygen at elevated temperature and oxidation have been discussed several places in this review (e.g., Blend, Engle, Tara3).

The foregoing evidence for the reactivity of the oxide superconductors makes it necessary to consider methods of passivation or protecting them from long-term degradation. An epoxy coating was found to provide some protection (Barns). Coating the surface with metals can be deleterious since metals such as Fe (Gaoz1, Hillz, Weave) and Ti (Meyel) react with the surface of LaSrCuO or YBaCuO. There is evidence for the passivation of the surface of LaSr\* with gold (Meyer).

## H. THERM

**Thermogravimetric analysis** was performed during a controlled atmosphere of oxygen concentration. The results were compared with procedures of other authors [John4, Leez9] and differential thermal analysis procedures.

## I. CHECKS

After a sample is cooled to a low temperature, the conductor is placed in a magnetic field. The field is then increased until the sample becomes a superconductor. The critical temperature of the sample is determined by the sharp change in the magnetic field. The critical temperature is  $-1/4\pi$ . This is the temperature of the superconductor. The fraction of the sample that is superconductor is determined by the fraction of the sample that is superconductor.

In addition to the chemical composition, the structure of the material is deduced from the XPS, electron spectroscopy probe that is used by investigators. The structure is much more complex than the back-scattered electrons, and the

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## H. THERMOGRAVIMETRIC ANALYSIS

Thermogravimetric analysis (TGA) consists of monitoring the weight of a sample during a heating or cooling cycle. For example, one might determine the oxygen content of a superconducting material by measuring its weight change in an oxidizing ( $O_2$  or air) or reducing (e.g., 4%  $H_2$  in Ar) atmosphere. Typical procedures consist of heating or cooling at  $20^\circ C/min$ . The relative accuracy of the method is about 0.005 (Ongz1). Many workers (e.g., Beye3, Hauck, Huan1, John4, Leez7, Maruc, Ohish, Ongz1, Tara7, Zhuzz) are now using TGA or differential thermal analysis (DTA) routinely during their sample preparation procedures.

## I. CHECKS ON QUALITY

After a sample has been prepared it is necessary to check its quality as a superconductor. Most investigators employ the four-probe resistivity check to determine whether it superconducts, and at what temperature it transforms to the superconducting state. A sharp, high  $T_c$  transition is an indicator of a high-quality sample. Another widely used quality control method is the determination of the magnetic susceptibility of the specimen. Good quality is indicated by a sharp, high  $T_c$  transition with both the flux exclusion and flux expulsion close to  $-1/4\pi$ . This is, in a sense, a more fundamental check on quality since the value of the susceptibility far below the transition temperature is a good indicator of the fraction of the sample that is superconducting (see Section III-D).

In addition to its superconducting properties, it is also of interest to know the chemical composition and the structure of the specimen. The nominal composition is deduced from the relative proportions of the various cations in the starting material. Chemical analysis and some more sophisticated techniques such as XPS, electrospectroscopic chemical analysis (ESCA), and an electron microprobe that is favorable for low-atomic-weight elements are applicable here. Most investigators only report the cation concentrations in the specimen. Oxygen content is much more difficult to determine, but is important to know. Rutherford back-scattering experiments (John1, Wuzz1, Wuzz4) can provide oxygen contents, and metallography characterizes grain sizes.

The structures of the oxide superconductors described in Chapter VI are easily checked by the X-ray powder pattern method. Many articles list the lattice constants  $a$ ,  $b$ ,  $c$  of samples and mention whether they are tetragonal ( $a = b \neq c$ ) or orthorhombic ( $a \approx b \neq c$ ). Narrow lines and the absence of spurious signals indicate a good, single-phase sample. Typical X-ray diffraction powder patterns for  $LaSr^*$  (Skelt) and  $YBa^*$  presented in Figs. V-3 and V-4, respectively, may be used to compare with patterns obtained from freshly prepared samples.

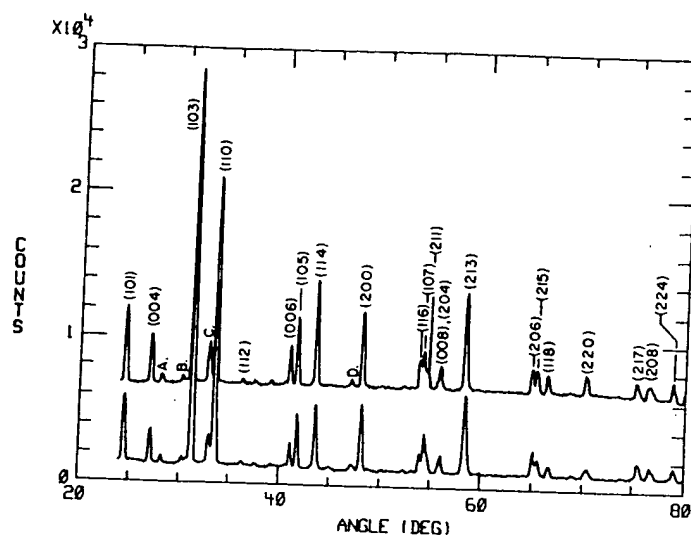


Fig. V-3. Room-temperature (upper curve) and 24-K (lower curve) X-ray diffraction powder patterns of  $(\text{La}_{0.925}\text{Ba}_{0.075})_2\text{CuO}_4$  (Skelt).

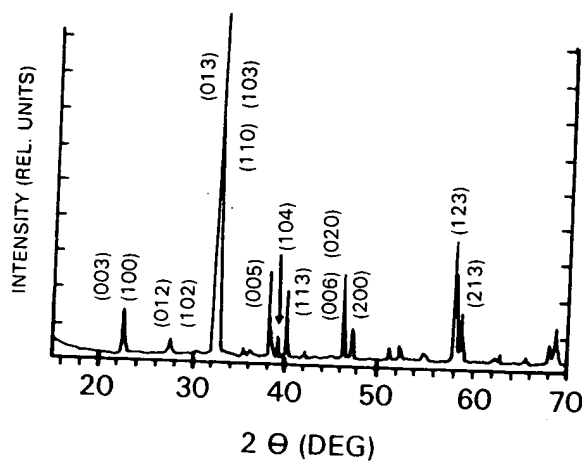


Fig. V-4. Room-temperature X-ray diffraction powder pattern of  $\text{YBa}_2\text{Cu}_3\text{O}_7$ . (Provided by C. Almasan, J. Estrada, and W. E. Sharp.)

## J. RESIST

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## J. RESISTIVITY MEASUREMENT

A measurement of the resistance  $R(T)$  or resistivity  $\rho(T)$  of a material versus the temperature is the principal technique employed to determine when a material becomes superconducting. The transition temperature manifests itself by a sharp drop in resistivity to zero. The simplest way to make this measurement is to apply a voltage across the sample and measure the current flow through it, but such a two-probe method (Baszy) is not very satisfactory, and is seldom used. Most resistivity determinations are made with the four-probe technique to be described below, although more sophisticated arrangements such as a six-probe method (Kirsch) can also be used. The fabrication of low-resistance contacts by silver glazing has been reported (Vand2). These researchers pointed out the importance of a low-contact resistance ( $\rho < 10 \mu\Omega/\text{mm}^2$  at 77 K) for making transport  $J_C$  measurements.

The specimen resistance as a function of temperature is generally determined in a suitable cryostat by attaching leads or electrodes to it in the standard four-probe configuration. Two leads or probes carry a known constant current  $I$  into and out of the specimen, and the other two leads measure the potential drop between two equipotential surfaces resulting from the current flow. For superconducting specimens the leads are often arranged in a linear configuration, with the contacts for the input current on the ends, and those for the measurement voltage near the center.

ray diffraction

$\text{u}_3\text{O}_7$ . (Provided

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